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Status Assessment of Toxic Chemicals: Polynuclear Aromatic Hydrocarbons

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Status Assessment of Toxic Chemicals

Polynuclear Aromatic Hydrocarbons

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16. ABSTRACT

This report identifies the origins, applications, environmental effects, and health effects of polynuclear aromatic hydrocarbons. Ways to reduce polynuclear aromatic hydrocarbon (PNA) emissions and problems associated with PNA derived effluents in the dye industry are discussed. Finally, various regulatory actions are listed and recommendations are made for further areas of study.

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STATUS ASSESSMENT OF TOXIC CHEMICALS:
POLYNUCLEAR AROMATIC HYDROCARBONS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of tris(2,3-dibromopropyl) phosphate. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

Polynuclear aromatic hydrocarbons (PNA's) enter the environment from natural and anthropogenic (man-made) sources. The main PNA's of commercial significance are phenanthrene, chrysene, and anthracene, which are refined from coal-derived chemicals. The 1974 capacity of phenanthrene, anthracene, and other PNA production facilities was 3.63×10^5 metric tons/yr.

Sources of anthropogenic PNA emissions include combustion or pyrolysis of fuels, processing of fuels, and manufacturing specialized organic chemicals. The majority of PNA emissions probably arise as pyrolysis products formed during combustion or heating of fossil fuels or natural products. Arithmetic mean concentrations of PNA's in air have been calculated as 0.4 μg/1,000 m^3 and 3 μg/1,000 m^3 for nonurban and urban locations, respectively, showing that urban concentrations tend to be much greater than nonurban concentrations.

Reduction of atmospheric PNA emissions from combustion sources can be achieved by proper control of combustion. Secondary combustion devices for flue gases could also reduce emissions. Since the major mode of transportation for PNA's appears to be adsorption onto particulates; control can be achieved by conventional particulate control devices, such as mechanical collectors or eletrostatic precipitators. Indications show that chlorination and ozonation of water supplies destroys PNA's, however, byproducts formed by chlorination may result in more toxic compounds.

Limitation of carbon monoxide and hydrocarbon emissions from motor vehicles have simultaneously and dramatically reduced PNA emissions. Similarly, compliance with existing regulations for incinerators, open burning, coal combustion, and coking operations could have corresponding benefits.

PNA derivatives employed as the basic structures in a number of important dyes and pigments represent a major source of water pollution. Large quantities of brines containing organic, highly colored materials are produced as wastes. Further information is needed on the magnitude of this problem and on the most effective controls.

Based upon the information presented in this report, several items need to be considered for further studies. Production quantities and sites of producer and use facilities should be identified. Effluents from organic dye and pigment manufacturing processes needs to be characterized and PNA concentrations quantified to determine the most effective controls. Transport methods in air and water should be studied so that the most effective controls may be achieved. Effects of long-term exposure of low-level PNA concentrations on humans should be determined and the associated population at risk identified. Finally, chlorination and ozonation of wastewaters should be reviewed for control efficiencies and for identification of possible toxic byproducts.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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CONVERSION FACTORS AND METRIC PREFIXES[a]

CONVERSION FACTORS

To convert from	to	Multiply by
Degree Celsius (°C)	Degree Fahrenheit	$t_F^\circ = 1.8\ t_C^\circ + 32$
Kilogram (kg)	Pound-mass (pound-mass avoirdupois)	2.204
Kilometer^2 (km^2)	Mile^2	3.860×10^{-1}
Meter^3 (m^3)	Foot^3	3.531×10^{1}
Meter^3 (m^3)	Gallon (U.S. liquid)	2.642×10^{2}
Metric ton	Pound-mass	2.205×10^{3}
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450×10^{-4}

METRIC PREFIXES

Prefix	Symbol	Multiplication factor	Example
Kilo	k	10^3	1 kg = 1×10^3 grams
Milli	m	10^{-3}	1 mm = 1×10^{-3} meter

[a] Standard for Metric Practice. ANSI/ASTM Designation: E 380-76$^\varepsilon$, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

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ERRATA SHEET

2/11/80

Please change the following:

page iii, paragraph 2, line 3, from "tris(2,3-dibromopropyl)"
to "polynuclear aromatic hydrocarbons".

SECTION 1

INTRODUCTION

Polynuclear aromatic hydrocarbons (PNA's) enter the environment from natural and man-made sources, including combustion or pyrolysis of fuels, processing of fuels, and manufacturing specialized organic chemicals. Increased levels of PNA's in urban air, in water, and in foods have caused rising concern due to the carcinogenic, mutagenic, and teratogenic properties of several PNA's.

There is a need to define the various sources from which PNA's may enter the environment, to establish consequent health and environmental effects, and to examine possible control strategies and current regulatory actions. This report provides a brief overview describing these items, with emphasis on PNA emission sources and resulting environmental levels.

SECTION 2

SUMMARY

Polynuclear aromatic hydrocarbons (PNA's) enter the environment from natural and man-made sources. These compounds occur naturally in plants and food, and are present in coal tar and creosote, which are derived from the breakdown of coal. The main PNA's of commercial significance, which are refined from coal-derived chemicals, are phenanthrene, chrysene, and anthracene. Essentially all commercial PNA's are used as reagents in organic synthesis. Table 1 highlights available information regarding PNA's.

PNA's are high melting, high boiling solids with low vapor pressures and low solubilities in water. Anthracene and phenanthrene can be refined from creosote, a distillation product of coal tar. The 1974 capacity of anthracene, phenanthrene, and other PNA production facilities was 3.63×10^5 metric tons/yr, and this capacity is expected to increase 10% by 1981.

Probably arising as pyrolysis products formed during combustion or heating of fossil fuels, PNA's are found in living plant and animal tissue, sediments, soils, air, and surface waters. Other man-made emission sources include processing of fuels and manufacturing specialized organic chemicals. Combustion sources are the largest contributors to PNA emissions.

There are many compounds derived from PNA's manufactured as specialty chemicals for use in organic dye and pigment manufacture. Although specific effluent rates are unknown for this industry, a problem exists in the area of liquid waste disposal since large quantities of brines containing organic, highly colored materials are produced as waste. In plants manufacturing PNA-based dyes, some of the organic materials present in the waste brines are probably PNA compounds.

PNA's seem to be transported in water and the atmosphere adsorbed on particulates and bacteria. Urban concentrations of PNA's in air tend to be 10 to 100 times greater than nonurban concentrations, with arithmetic mean concentrations of 0.4 $\mu g/1{,}000\ m^3$ for nonurban locations and 3 $\mu g/1{,}000\ m^3$ for urban locations. Essentially insoluble in water, PNA's may exist in water in association with other organic matter or colloids, such as those formed by detergents.

TABLE 1. POLYNUCLEAR AROMATIC HYDROCARBONS

Emission source	Extent of problem: Air emission quantity[a] (metric tons/yr)	Extent of problem: Population exposed	Control method	Regulatory action
Combustion				
Coal	376.1	Indication of widespread exposure because PNA's exist in all phases of the environment. Urban concentrations are 10 to 100 times greater than non-urban concentrations. Persons working with or using fossil fuel-derived products are exposed to high PNA levels.	PNA's from combustion sources may be controlled by increasing air-to-fuel ratios or using secondary combustion devices on flue gases. Conventional particulate control methods could help reduce PNA transport.	Compliance with existing regulations for incinerators, open burning, coal combustion and coking operations could significantly reduce emissions. Specific control regulations are not believed to be warranted or practical.
Oil	1.4			
Gas	1.1			
Refuse burning	18.5			
Catalytic cracking of petroleum	17.1			
Asphalt road mix	9.07×10^{-6}			
Asphalt air blowing	$<4.35 \times 10^{-5}$			
Motor vehicles	18.7		Chlorination and ozonation of water supplies are believed to destroy PNA's but more toxic byproducts could be formed.	One hundred and twenty-nine chemicals including 13 PNA's have recently been designated priority pollutants under the Federal Water Pollution Control Act.
Dye and pigment manufacture	-			

[a] Emissions given in metric tons/yr of benzo(a)pyrene.

Air emissions of PNA's from combustion sources can be reduced by increasing air-to-fuel ratios, or with secondary combustion devices for flue gases. Particulate matter, which appears to a method of transport for PNA's in the environment, may be controlled by conventional methods, such as mechanical collectors or electrostatic precipitators, thus aiding in reducing PNA emissions. Indications are that chlorination and ozonation of water supplies destroys PNA's; however, byproducts much more toxic than the original compounds may be produced in chlorination.

Limitation of carbon monoxide and hydrocarbon emissions from motor vehicles has simultaneously and dramatically reduced PNA emissions from these sources. Control regulations designed specifically for PNA's are not considered practical, but compliance with existing regulations for incinerators, open burning, coal combustion, and coking operations could significantly reduce emissions. Consideration is being given to establishing revised standards for coke oven emissions under the Clean Air Act. Documentation of physical and chemical behavior, health and environmental effects, and sources and environmental levels for 65 chemicals and classes, including PNA's, was scheduled to be published by July 1977. Subsequently, appropriate water quality criteria, effluent guidelines, toxic pollutant standards, and/or pretreatment requirements will be established under the Federal Water Pollution Control Act in accordance with a court-approved schedule.

Based upon the information presented in this report, the following items need to be considered for future studies:

- Production quantities and locations of user and manufacturer facilities should be identified for all major PNA's.
- Effluents from organic dye and pigment manufacturing processes should be characterized and PNA concentrations quantified to determine the most effective controls.
- PNA transport methods should be studied so that efficient emission and effluent pollutant control may be realized.
- Human health effects of long-term, low-level exposure should be determined.
- Population risking exposure to PNA's should be quantified.
- Chlorination and ozonation of wastewaters should be reviewed for control efficiencies and for identification of possible toxic byproducts.
- PNA atmosphere and environmental persistence.

SECTION 3

SOURCE DESCRIPTION

Polynuclear aromatic hydrocarbons (PNA's) enter the environment from natural and anthropogenic (man-made) sources. PNA's are not manufactured as synthetic organic chemicals. These compounds occur naturally in plants and food, and are present in coal tar and creosote, which are derived from the breakdown of coal. Since the form of PNA's in coal is unclear, it is not known whether it is anthropogenic or natural in origin. Phenanthrene, chrysene, and anthracene, which are refined from coal derived chemicals, are the main PNA's of commercial significance. Essentially all commercial PNA's are used as reagents in organic synthesis.

CHEMICAL AND PHYSICAL PROPERTIES

Chemical nomenclature for 12 selected PNA's is listed in Table 2 (1, 2). Polynuclear aromatic hydrocarbons are all high melting, high boiling solids. Tables 3 and 4 summarize specific properties of selected PNA's (3-9). As shown in Table 4, vapor

---

(1) Radding, S. B., T. Mill, C. W. Gould, D. H. Liv, H. L. Johnson, D. C. Bomberger and V. C. Fojo. The Environmental Fate of Selected Polynuclear Aromatic Hydrocarbons. EPA 560/5-75-009, U.S. Environmental Protection Agency, Washington, D.C., February 1976. 131 pp.

(2) Patterson, A. M., L. T. Capell, and D. F. Walker. The Ring Index. A List of Ring Systems Used in Organic Chemistry. American Chemical Society, Washington, D.C., 1960. 1425 pp.

(3) International Agency for Research on Cancer, "Monograph on the Evaluation of Carcinogenic Risk of the Chemical to Man: Certain Polycyclic Aromatic Hydrocarbons and Heterocyclic Compounds," World Health Organization, Geneva, Switzerland, 1973, Volume 3.

(4) Hansch, C. (1975), private communication, Pomona College, Pomona, California.

(5) Fieser, L. F. and A. M. Seligman (1935), "The Synthesis of Methycholanthrene," J. Amer. Chem. Soc. 57, 942-46.

(6) "Handbook of Chemistry and Physics," 45th Ed., Chemical

(continued)

TABLE 2. NAMES AND SYNONYMS FOR 12 PNA's (1, 2)

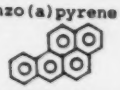
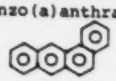
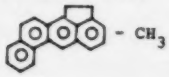
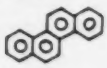
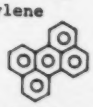
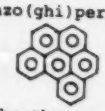
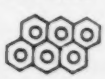
Common name	Synonyms
Benzo(a)pyrene 	3,4-Benzpyrene BP BAP 3,4-Benzopyrene
Benzo(a)anthracene 	1,2-Benzanthracene Benzanthrene Benzo(b)phenanthrene 2,3-Benzophenanthrene Tetraphene 1,2-Benz(a)anthracene
Methylcholanthrene 	Cholanthrene, 3-methyl- 20-MC MC 3-MC 20-Methylcholanthrene 3-Methylcholanthrene
Chrysene 	1,2-Benzphenanthrene
Anthracene	Paranaphthalene
Phenanthrene	None
Benzo(e)pyrene	4,5-Benzopyrene 1,2-Benzopyrene
Perylene 	Dibenz(de,kl)anthracene
Benzo(ghi)perylene 	1,12-Benzoperylene
Anthanthrene 	Dibenzo(def,mno)chrysene Dibenzo(cd,jk)pyrene
Coronene	Dibenzo(ghi,pqr)perylene
Fluoranthene	Benz(a)acenaphthylene 1,2-Benzoacenaphthylene

TABLE 3. PHYSICAL PROPERTIES OF SIX PNA's

PNA	Mol. formula	Mol. weight (g/mole)	M.P. °C	B.P. °C/Pa	Log partition coefficient[a]
Benzo(a)pyrene	$C_{20}H_{12}$	252.30	179 (3)	311/1.33 x 10^3 (3)	6.04 (4)
Benzo(a)anthracene	$C_{18}H_{12}$	228.28	160 (3)	400/1.01 x 10^5 (3)	5.61 (4)
Methylcholanthrene	$C_{21}H_{16}$	268.34	179 (5)	N.A.[b]	5.83 (4)
Chrysene	$C_{18}H_{12}$	228.28	256 (3)	448/1.01 x 10^5 (3)	5.61 (4)
Anthracene	$C_{14}H_{10}$	178.23	216 (4)	340/1.01 x 10^5 (6)	4.45 (7)
Phenanthrene	$C_{14}H_{10}$	178.23	101 (4)	340/1.01 x 10^5 (6)	4.46 (7)

[a]Partition Coefficient = the solubility of PNA in 1-octanol divided by its solubility in water.

[b]Not available.

TABLE 4. VAPOR PRESSURE AND VAPOR CONCENTRATION OF SELECTED PNA's AT 25°C

PNA	Vapor pressure (Pa)[a]	Vapor concentration[b] ($\mu g/10^3$ m^3)	Vapor concentration[b] (moles/m^3)
Benzo(a)pyrene	7.32×10^{-7}	75	2.97×10^{-11}
Benzo(a)anthracene	1.47×10^{-5}	1,333	5.84×10^{-11}
Benzo(e)pyrene	7.38×10^{-7}	75	2.97×10^{-11}
Benzo(k)fluoranthrene	1.28×10^{-6}	13	5.15×10^{-12}
Benzo(ghi)perylene	1.37×10^{-8}	1.5	5.43×10^{-13}
Coronene	1.96×10^{-10}	0.02	6.66×10^{-15}
Anthracene	2.60×10^{-2}	1.87×10^7	1.05×10^{-5}
Phenanthrene	9.06×10^{-2}	6.51×10^7	3.65×10^{-5}
Pyrene	9.13×10^{-5}	74,400	3.68×10^{-8}

[a]All data from Reference 8 except for anthracene and phenanthrene, which is from Reference 9. The equations given in the references were determined from data obtain at 100-300°C or higher; vapor pressures at 25°C are extrapolations.

[b]Calculated from data in Reference 8 except for anthracene and phenanthrene which were calculated from equations in Reference 9 and the ideal gas law.

(continued)

(6) Rubber Co., Cleveland, Ohio, 1964.

(7) Leo, A., C. Hansch, and D. Elkins (1971), "Partition Coefficients and Their Uses," Chem. Rev. 71(6), 525-616.

(8) Pupp, C., R. C. Lao, J. J. Murray, and R. F. Pottie (1974), "Equilibrium Vapor Concentrations of Some Polycyclic Aromatic Hydrocarbons, Arsenic Trioxide (As_4O_6) and Selenium Dioxide, and the Collection Efficiencies of these Air Pollutants," Atmos. Environ. 8(9), 915-25.

(9) Jordan, T. E., "Vapor Pressures of Organic Compounds," Interscience Publishers, Inc., New York, 1954.

pressures are extremely low. Solubilities of PNA's in water generally appear to be less than 10^{-10} molar. These compounds undergo the reactions of simple aromatics, in addition to some reactions peculiar to PNA's as a class. They are subject to oxidation and yield quinones, diols, peroxides, and ring cleavage products. Alkylated PNA's are more reactive toward electrophilic agents, with reactivity increasing with ring number (1).

PRODUCTION AND USE OF POLYNUCLEAR AROMATIC HYDROCARBONS

Anthracene is the only PNA of commerce refined from fossil fuel sources. While quantities refined were not found, several coal tar resin producers, who may refine anthracene, are presented in Table 5 (10).

TABLE 5. COAL TAR RESIN PRODUCERS (10)

Chemfax, Inc.	Gulfport, MS
The Goodyear Tire & Rubber Co. Chem. Div.	Beaumont, TX
Hercules, Inc. Organics Dept.	Baton Rouge, LA
	Clairton, PA
	West Elizabeth, PA
Neville Chem. Co.	Anaheim, CA
	Neville Island, PA
Northwest Indust., Inc., Velsicol Chem. Corp., subsidiary	Marshall, IL
Reichhold Chems., Inc. Newport Div.	Gulfport, MS
Schenectady Chems., Inc.	Rotterdam Junction, NY

Anthracene and phenanthrene can be refined from creosote, which is produced by distillation of coal tar. A number of distillate oils are produced in the distillation of coal tar and creosote is a mixture of these oils. Creosote production may be represented by the schematic shown in Figure 1 (11). Creosote is

(10) 1977 Directory of Chemical Producers. Stanford Research Institute, Menlo Park, California. 1977. p. 782.

(11) von Rümker, R., E. W. Lawless, and A. F. Meiners. Production, Distribution, Use and Environmental Impact Potential of Selected Pesticides (PB 238 795). Council on Environmental Quality, Washington, D.C., March 1974. 439 pp.

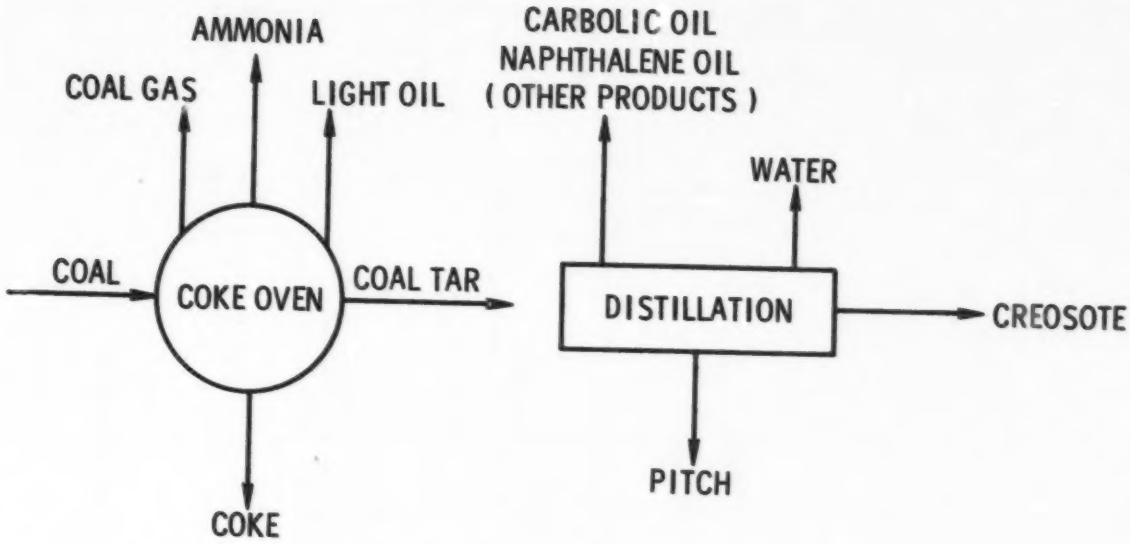


Figure 1. Production schematic for creosote (11).

then washed with water, and solid crude anthracene is separated in filters and centrifuges as shown in Figure 2 (12). The crude product is then recrystallized from furfural. Solids separation and drying steps produce refined anthracene product.

In 1974, the capacity of phenanthrene, anthracene, and other PNA production facilities was 3.63×10^5 metric tons/yr and this capacity is expected to increase 10% by 1981 (13). Actual current production data were not available. However, since the majority of PNA's are produced at steel making facilities, eight steel companies planning to expand steel production by 1981 at 11 sites are listed in Table 6 (13).

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(12) Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Major Organic Products Segment of the Organic Chemicals Manufacturing Point Source Category, EPA 440/1-74-009-a, U.S. Environmental Protection Agency, Washington, D.C., 1974.

(13) Cooper, F. D. Coke and Coal Chemicals. In: Minerals Yearbook 1974, Volume 1. Metals, Minerals, and Fuels. U.S. Government Printing Office, Washington, D.C., 1976. p 447.

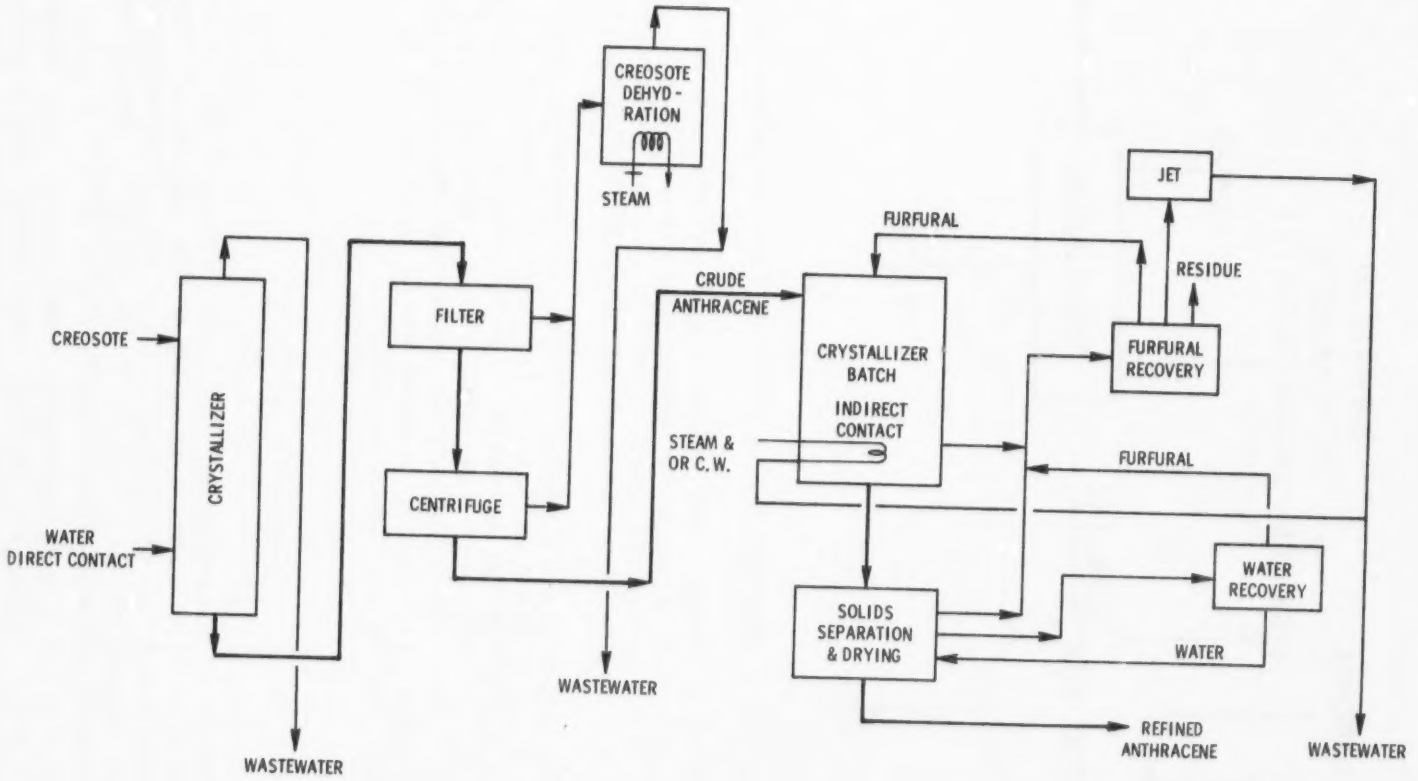

Figure 2. Anthracene refining flow diagram (12).

TABLE 6. STEEL COMPANIES EXPANDING PNA PRODUCTION (13)

Company	Location	Approximate start-up date
Armco Steel Corp.	Middletown, OH	July 1976
Bethlehem Steel Corp.	Bethlehem, PA	Mid-1975
Inland Steel Co.	East Chicago, IN	1978
Jones & Laughlin Steel Corp.	Aliquippa, PA	Mid-1975
	Aliquippa, PA	Not contracted
Lykes-Youngstown Corp.	Indiana Harbor, IN	Mid-1977
Republic Steel Corp.	Cleveland, OH	1976
	Warren, OH	1978
United States Steel Corp.	Gary, IN	Late 1975
	Gary, IN	Late 1976
Wheeling-Pittsburg Steel Corp.	Follansbee, WV	Mid-1977

Table 7 presents a partial list of uses for three of the most important PNA's (14).

TABLE 7. MAJOR USES OF THREE PNA's (14)

Compound	Uses
Anthracene	Dyes; alizarin; phenanthrene; carbazole; anthraquinone; calico printing; component of smoke screens; scintillation counter crystals; reagent in organic semiconductor research
Chyrsene	Organic synthesis
Phenanthrene	Dye stuffs; explosives; drug synthesis; biochemical research; phenanthrene-quinone

(14) Hawley, Gessner, G., Ed., The Condensed Chemical Dictionary, 8th Ed., New York, Van Nostrand Reinhold Co., 1971.

SECTION 4

ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

ENVIRONMENTAL SIGNIFICANCE

PNA's are widely distributed in the environment. They are found in living plant and animal tissue, sediments, soils, air, and surface waters. The majority of PNA's probably arise as pyrolysis products formed during combustion or heating of fossil fuels. The major environmental transport mode is as particulate in air or water, due primarily to low vapor pressures and virtual insolubility in water. Presently used methods of analysis for estimating airborne concentrations of PNA's however, may seriously underestimate the concentrations of some relatively volatile PNA's such as pyrene, anthracene, and benzo(a)anthracene (1).

Sources

PNA's enter the environment from natural and anthropogenic sources. Anthropogenic PNA emissions may occur from combustion or pyrolysis of fuels, processing of fuels, and manufacturing of specialized organic chemicals.

Several potential sources of PNA emissions have been monitored. Emission estimates for these sources are presented in Table 8 (15). Combustion sources are the largest contributors to PNA emissions. Sampling and analysis data for these combustion sources are presented in Tables 9 through 15 (15).

PNA emissions from petroleum refining sources have been studied; sampling and analysis results are presented in Table 16 (16). Table 17 lists emissions of PNA from catalytic regeneration in petroleum catalytic cracking (15).

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(15) Hangebrauck, R. P., et al., Sources of Polynuclear Hydrocarbons in the Atmosphere, 999-AP-33, Public Health Service, 1967.

(16) Samedov, I. G. and A. S. Kurbanov, "Pollution of the Air with Carcinogenic Substances by Baku Petroleum Refineries," Azerbaydzhanskiy Medit. Zh. 28 (11), 62-67 (1971).

TABLE 8. ESTIMATES OF ANNUAL BENZO(a)PYRENE EMISSIONS FROM VARIOUS SOURCES (15)

Source	Estimated annual emission (metric tons)
Coal combustion	
Residential	
Hand stoked	362.9
Underfeed	8.8
Commercial	2.5
Industrial	0.5
Power plants	1.4
Oil combustion	1.4
Gas combustion	1.1
Refuse burning	
Municipal incineration	0.1
Commercial incineration	4.4
Open burning-municipal	4.4
Grass, leaves	4.4
Auto components	5.2
Catalytic cracking of petroleum	
FCC[a] - no carbon monoxide boiler	0.19
FCC[b] - with carbon monoxide boiler	0.010
HCC[b] - no carbon monoxide boiler	5.1
HCC[c] - with carbon monoxide boiler	0.0022
TCC[c] - air lift - no carbon monoxide boiler	11.8
TCC - air lift - with carbon monoxide boiler	<0.0026
TCC - bucket lift - no carbon monoxide boiler	0.0037
Asphalt road mix	9.07×10^{-6}
Asphalt air blowing	$<4.35 \times 10^{-5}$
Motor vehicles	
Gasoline automobiles	7.8
Gasoline trucks	>9.1
Diesel	1.8

[a]Fluid catalytic cracking.

[b]Houdriflow catalytic cracking.

[c]Thermofor catalytic cracking.

TABLE 9. EMISSIONS OF PNA FROM COAL-FIRED PLANTS (15)

Type of unit	Emissions in $\mu g/10^3$ J fuel								
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Perylene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Phenanthrene	Fluoranthene
Pulverized coal (vertically-fired, dry-bottom furnace)	18 - 123	70 - 218	39 - 75	22	79				80 - 389
Pulverized coal (front-wall-fired, dry-bottom furnace)	16 - 20	152 - 190	52		13			190	12 - 152
Pulverized coal (tangentially-fired, dry-bottom furnace)	123	133	80	67	142	4.6	6.7	30	370
Pulverized coal (opposed-, downward inclined burners; wet bottom furnace)	20 - 133	37 - 114	68 - 398		142 - 1,042		7.7 - 88		52 - 199
Crushed coal (cyclone-fired, wet-bottom furnace)	72 - 351	237 - 1,706	104 - 645	32	34 - 341		10		42 - 104
Spreader stoker (traveling grate)	<14 - 23	20 - 56	58				9.0		20 - 56

NOTE: Blanks indicate data not available.

TABLE 10. EMISSIONS OF PNA FROM COAL-FIRED RESIDENTIAL FURNACES (15)

Firing method	Emissions, $\mu g/10^9$ J fuel									
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Perelene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
Underfeed stokers	3,600 - 76,780	7,300 - 284,360	5,120 - 55,920	407 - 7,490	550 - 57,800	1,230 - 5,780	1,140 - 3,890	1,230 - 66,350	27,500 - 578,200	44,550 - 312,800
Hand stoked	379,150 - 3,127,960	568,720 - 8,625,600	94,800 - 1,421,800	56,870 - 331,750	284,360 - 2,085,300	85,300 - 464,500	28,440 - 91,950	379,150 - 2,748,800	947,900 - 7,109,000	947,900 - 10,426,500

NOTE: Blanks indicate data not available.

TABLE 11. EMISSIONS OF PNA FROM INTERMEDIATE-SIZED COAL-FIRED UNITS (15)

Firing method	Emissions, $\mu g/10^9$ J fuel									
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Perelene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
Pulverized	30	227	87					350		
Chain grate stoker	35	370	123							645
Spreader stoker	25	560	330				25			340
Underfeed stokers	114 - 9,500	1,610 - 15,160	218 - 7,500	1,516	4,260	275	313	805	948 - 9,480	3,030 - 36,000

NOTE: Blanks indicate data not available.

TABLE 12. EMISSIONS OF PNA FROM INTERMEDIATE AND SMALL-SIZED OIL-FIRED UNITS (15)

Firing method	Emissions, μg/10^9 J fuel						
	Benzo(a)-pyrene	Pyrene	Benzo(ghi)-perylene	Coronene	Anthan-threne	Phenan-threne	Fluoran-thene
Steam atomized	<19-45	46-284				1,700	53-256
Low pressure air atomized	853	5,780	285	1,990	3,700	3,320	1,800
Pressure atomized	<38-<57	14-1,700				8,440	72-4,470
Vaporized	<95	1,140					14,200

NOTE: Blanks indicate data not available.

TABLE 13. EMISSIONS OF PNA FROM INTERMEDIATE AND SMALL-SIZED GAS-FIRED UNITS WITH PREMIX BURNERS (15)

Emissions, μg/10^9 J fuel						
Benzo(a)-pryene	Pyrene	Benzo(e)-pyrene	Benzo(ghi)-perylene	Anthan-threne	Coronene	Fluoran-thene
<19 - 256	15,170	1,420	2,180	69	787	7,580

TABLE 14. EMISSIONS OF PNA FROM INCINCERATION AND OPEN BURNING (15)

Type of Unit	Emissions, μg/kg refuse charged									
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Pery-lene	Benzo(ghi)-perylene	Anthan-threne	Coronene	Anthra-cene	Phenan-threne	Fluoran-thene
Municipal:										
227 metric ton/day, multiple chamber	0.165	17.6	0.75				0.53			22
45 metric ton/day, multiple chamber, after scrubber	0.096	4.6	1.28		1.4		1.39			7.3
Commercial:										
4.8 metric ton/day, single chamber	117	705	100	6.8	200	15	46	103	308	485
2.7 metric ton/day, multiple chamber	573	9,250	573	132	1,920	175	463	190	130	8,600
Open burning:										
Municipal refuse	337	1,760	230		155					1,600
Grass clippings, leaves, branches	346	1,720	155	37		160	26			1,100
Automobile components	28,600	74,900	14,500	2,600	19,600	2,200	2,400	3,130	21,350	53,750

NOTE: Blanks indicate data not available.

TABLE 15. EMISSIONS OF PNA FROM MOTOR VEHICLES (15)

Type of vehicle	Emissions, 10^{-9} g/vehicle meter									
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Pery-lene	Benzo(ghi)-perylene	Anthan-threne	Coronene	Anthra-cene	Phenan-threne	Fluoran-thene
Automobiles	1.8 - 20.8	8.0 - 212	2.9 - 19.6	0.17 - 2.2	4.2 - 90	0.19 - 2.83	2.5 - 39.7	0.65 - 7.9	2.7 - 57	4.2 - 145
Trucks	>1.6 - 80	255 - 930	>2.2 - 65	0.52 - 12	57 - 300	0 - 73	24 - 150	4 - 168	162 - 640	137 - 610

TABLE 16. EMISSIONS OF PNA FROM PETROLEUM REFINING (16)

Process	Emissions, µg/100 m³[a]	
	Benzo(a)-pyrene	Benzo(ghi)-perylene
Straight run distillation	0.015	0.11
Pyrolysis	0.30	0.170
Asphalt production	0.74	1.58
Petroleum coke production	25.5	0.4
Petroleum products purification	0.024	-[b]

[a] Mean values of multiple samples.

[b] Not available.

TABLE 17. EMISSIONS OF PNA FROM CATALYST REGENERATION IN PETROLEUM CATALYTIC CRACKING (15)

Type of unit	Emissions, µg/m³ oil charges									
	Benzo(a)-pyrene	Pyrene	Benzo(e)-pyrene	Perylene	Benzo(ghi)-perylene	Anthanthrene	Coronene	Anthracene	Phenanthrene	Fluoranthene
FCC:[a]										
Regenerator outlet	0.7 - 73	6.4 - 4,450	1.7 - 572		24 - 67				63,560	7.0 - 3,180
Carbon monoxide boiler outlet	1.7 - 3.4	3.9 - 26	2.9 - 3.3		8.8			330		3.2 - 13
HCC:[b]										
Regenerator outlet	32,600 - 36,700	20,700 - 20,800	20,800 - 60,400	5,400	47,700 - 60,400	2,380 - 2,860	1,780 - 4,130	146 - 318	3,340 - 4,600	1,320 - 1,810
TCC:[c]										
Air lift, regenerator outlet	8,900 - 19,100	21,000 - 41,300	8,900 - 19,100	875 - 1,590	7,000 - 11,450	205 - 700	57	1,640 - 1,685	52,500 - 56,000	1,685 - 4,610
TCC:										
Brucket lift, regenerator outlet	5	46 - 57	13							9 - 17

NOTE: Blanks indicate data not available.

[a] Fluid catalytic cracking.

[b] Houdriflow catalytic cracking.

[c] Thermofor catalytic cracking.

PNA's, in the form of particulates, can be emitted to the atmosphere from coking operations. Particulate matter collected from the air in the vicinity of a coke oven and steel mill has been analyzed and the results are shown in Table 18 (15). The major sources of atmospheric emissions from the coke and steel industry are slot-type coke ovens and oxygen-lanced open hearth furnaces. Beehive ovens have higher emission rates, but they are seldom used in the industry. PNA's are also found in coal tars (17).

(17) Lowry, H. H., Ed., Chemistry of Coal Utilization, 2 Vols. and supplementary volume, N.Y., Wiley, 1945, 1963 (supplementary volume).

TABLE 18. CONCENTRATION OF PNA IN PARTICULATES IN AIR NEAR STEEL AND COKE PLANT (15)

Compound	Concentration, g/1,000 m^3 air
Benzo(a)pyrene	8.6
Pyrene	6.6
Benzo(e)pyrene	4.1
Perylene	1.0
Benzo(ghi)perylene	7.1
Anthanthrene	0.83
Coronene	0.44
Anthracene	2.4
Fluoranthene	3.2

Processing of coal tar could result in PNA emissions in both gaseous and liquid or semi-liquid form.

Asphalt blowing and hot-mix asphalt plants are potential PNA emission sources. The results of a sampling and analysis program for these two sources are shown in Tables 19 and 20 (15). Carbon black plants are also potential emitters of PNA's (15, 18). Table 21 presents an analysis of collected particulate matter in the vicinity of a carbon black plant (15).

TABLE 19. EMISSIONS OF PNA FROM ASPHALT BLOWING (15)

Compound	Emissions, µg/1,000 m^3 (211.1°C, 1 x 10^5 Pa)
Pyrene	3,100,000
Benzo(a)pyrene	<4,000
Anthracene	220,000

(18) Todd, Robert G., Direct Identification of Polycyclic Aromatic Hydrocarbons from Carbon Black, Masters Thesis, University of Oklahoma, Norman, Oklahoma, 1970.

TABLE 20. EMISSIONS OF PNA FROM ASPHALT HOT-ROAD MIX PLANTS (15)

Compound	Emissions, μg/1,000 m^3 (211.1°C, 1 x 10^5 Pa)
Pyrene	3,000
Benzo(a)pyrene	<100
Anthracene	1,400
Fluoranthene	2,500

TABLE 21. CONCENTRATION OF PNA IN PARTICULATES IN AIR NEAR CARBON BLACK PLANT (15)

Compound	Concentration, μg/1,000 m^3 air
Benzo(a)pyrene	0.035 - 0.58
Pyrene	0.15 - 0.33
Benzo(e)pyrene	0.18 - 0.76
Perylene	0.03
Benzo(ghi)perylene	0.37 - 0.16
Coronene	0.16 - 0.59
Fluoranthene	0.07 - 0.43

There are compounds derived from PNA's manufactured as specialty chemicals for use in organic dye and pigment manufacture. A few of the dyes whose chemical structures are based on PNA's are azine dyes, alizarin, pyranine, pyranthrone, benzanthrone, isoviolanthrone, and perylene. Although specific emission rates and data are largely unknown for this industry, an industry-wide problem exists in the area of liquid waste disposal. Large quantities of brines containing organic, highly colored materials are produced as waste. In plants manufacturing PNA-based dyes, some of the organic materials present in the waste brines most likely are PNA compounds.

Emissions of PNA's have been measured from other industries. Table 22 contains benzo(a)pyrene emission data for some of these industries (19-21).

(19) Zdrazil, J. and P. Picha (1965), "Carcinogenic Hydrocarbons, Especially 3,4-benzopyrene, in the Atmosphere of Foundries," Slevarenstvi 13, 198-9.

(20) Olsen, D. A., J. L. Haynes (1969), "Air Pollution Aspects of Organic Carcinogens," Report No. PB-188 090, 131 p.

(21) Bolotova, M. N., Ya. S. Davydov, and N. G. Nikishina (1967), (continued)

TABLE 22. MISCELLANEOUS INDUSTRIAL SOURCES OF PNA'S

Industry	Emissions	Reference
Foundry (casting operations)	1 - 3 mg BaP[a]/$10^3 m^3$	19
Aluminum plant	10 kg BaP[a]/day 0.26 mg BaP[a]/m^2-day	20
Fiberboard works-pitch boiling plant	0.2 mg BaP[a]/$10^3 m^3$ on premises 0.1 mg BaP[a]/$10^3 m^3$ at 100 m 0.05 mg BaP[a]/$10^3 m^3$ at 500 m	21
Carborundum	0.08 mg BaP[a]/$10^3 m^3$	21
Vinyl phonograph records plant	5.2 mg BaP[a]/$10^3 m^3$	21
Rubber products plant	0.05 - 0.02 mg BaP[a]/$10^3 m^3$ (dependent on distance)	21

[a]Benzo(a)pyrene

Environmental Levels

Air--
Urban concentrations of PNA's in air tend to be 10 to 100 times greater than nonurban concentrations. An arithmetic mean concentration has been determined: 0.4 µg/1,000 m^3 for nonurban locations, 3 µg/1,000 m^3 for urban locations (20). Winter levels are usually higher than summer levels. This phenomenon may be due to both lower photo-oxidation rates and increased use of fossil fuels for space heating. Table 23 contains some data for atmospheric levels of PNA's as a function of season (3, 20). Traffic variations also cause variations in PNA concentrations. The range in values corresponding to traffic variations is shown in Table 24 (3). Traffic contributes from 5% to 42% to the level of PNA's in air (22).

(continued)

(21) "Basic Industrial Sources of the Carcinogenic Hydrocarbon; Benzo(a)pyrene," Med. Zh. Uzb. No. 11, 51-4.

(22) Sawicki, E. (1967), "Airborne Carcinogens and Allied Compounds," Arch. Environ. Health 14 (1), 46-53.

TABLE 23. ATMOSPHERIC CONCENTRATION OF PNA'S IN SEVERAL CITIES

	Winter, $\mu g/1{,}000\ m^3$	Summer, $\mu g/1{,}000\ m^3$	Reference
Benzo(a)pyrene	0.6 - 104	0.03 - 4	3
	26 (14 U.S. Cities)	1.9 (14 U.S. Cities)	20
Chyrsene	20 - 361	2.5 - 3.6	3
Benz(a)anthracene	94 (Siena)	1.6 (Siena)	3
	361 (Bochun)	136 (Pittsburgh)	

TABLE 24. VARIATIONS OF PNA CONCENTRATION WITH TRAFFIC (3)

PNA	Concentration, $\mu g/1{,}000\ m^3$
Benzo(a)pyrene	2.5 - 6.5
Chrysene	1.8 - 13.3
Benz(a)anthracene	0.6 - 13.7

PNA's seem to be transported in the atmosphere adsorbed on particulates and bacteria. An analysis of particulate matter from six cities is given in Table 25 (3).

TABLE 25. PNA'S IN ORGANIC PARTICULATE MATTER FROM SIX CITIES (3)

PNA	Concentration, $\mu g/g$
Benzo(a)pyrene	110 - 670
Chrysene	150 - 490
Benz(a)anthracene	43 - 280

Water--
PNA's are essentially insoluble in water. They may exist in water in association with other organic matter or colloids, such as those formed by detergents. They are probably transported to the waterways adsorbed on particles or bacteria. Table 26 presents concentrations of carcinogenic PNA's found in water systems (23). Another study of water contamination by three specific PNA's resulted in the data shown in Table 27 (3).

TABLE 26. CARCINOGENIC PNA CONCENTRATIONS IN WATER SOURCES (23)

Source	mg/m^3
Ground water	0.001 - 0.1
Treated river and lake water	0.01 - 0.025
Surface water	0.025 - 0.100
Surface water, strongly contaminated	>0.100

TABLE 27. PNA CONCENTRATIONS IN WATER (3)

PNA	Drinking water, mg/m^3	Surface water, mg/m^3
Benzo(a)pyrene	0.0001 - 0.023	0.0006 - 0.114
Chrysene	-[a]	0.0118 - 0.038
Benz(a)anthracene	0.001 - 0.023	0.0043 - 0.185

[a]Not available.

Soils--
Levels of three PNA's found in soils from different locations are presented in Table 28 (3). The PNA compounds may settle on the soil where they are absorbed by microorganisms or plants or are decomposed by bacteria. There is a natural background level of PNA's in soil, probably due to production by plants and microorganisms.

TABLE 28. CONCENTRATIONS OF PNA IN VARIOUS SOILS (3) (µg/kg)

Soil source	Benzo(a)-pyrene	Chrysene	Benz(a)-anthracene
Forest	<1,300	-[a]	5 - 206
Nonindustrial	0 - 127	-[a]	-[a]
Towns and vicinities	0 - 939	-[a]	-[a]
Soil near traffic	<2,000	-[a]	1,500
Near oil refinery	200,000	-[a]	-[a]
Near airfield	785	-[a]	-[a]
Polluted by coal tar pitch	650,000	600,000	2,500,000

[a]Data not available.

(23) Andelman, J. B., M. J. Suess (1970), "Polynuclear Aromatic Hydrocarbons in the Water Environment," World Health Organization 43, 479-508.

Plants, Food, and Beverages--
The concentration of benzo(a)pyrene is 10 µg/kg to 50 µg/kg in plants, 2 µg/kg to 10 µg/kg in dried bacteria, and 103 µg/kg to 270 µg/kg in tobacco leaves (1).

PNA's have been determined in many foods; some of the concentrations found are listed in Tables 29, 30, and 31 (3, 23-28). Table 32 contains concentrations of PNA's as determined in beverages (3, 25).

TABLE 29. PNA CONCENTRATIONS IN CEREALS AND POTATOES (µg/kg)

PNA	Cereals	Potatoes	Reference
Benz(a)anthracene	In general 0.4 - 6.8	-[a]	3
Chyrsene	In general 0.8 - 14.5	-[a]	3
Benzo(a)pyrene	In general 0.25 - 0.84	Peelings 0.36 Tubers 0.09	24
	Barley, Wheat, Rye 0.2 - 4.1		25

[a]Not available.

(24) Shabab, L. M. and Y. L. Cohan (1972), "Contents of Benzo(a)-pyrene in Some Crops," Arch. Geschwulstforsch. 40 (3), 237-43.

(25) Grimmer, G. (1968), "Carcinogenic Hydrocarbons in the Human Environment," Deut. Apoth.-Ztg. 108(16),529-33.

(26) Grimmer, G., A. Hildebrandt (1965b), "Content of Polycyclic Hydrocarbons in Different Vegetables. III. Hydrocarbons in the Human Surroundings," Deut. Lebensm.-Rundschau 61(8), 237-9.

(27) Gorelova, N. D., P. P. Dikun, L. D. Kostenko, O. P. Gretskaya, and A. V. Emshanova (1971), "Detection of the Possible Presence of 3,4-benzopyrene in Fresh Fish," Novosti Onkol., 8-12.

(28) Wierzchowski, J. and R. Gajewska (1972), "Determination of 3,4-benzopyrene in Smoked Fish," Bromatol. Chem. Toksykol. 5(4), 481-6.

TABLE 30. PNA CONCENTRATIONS IN VEGETABLES AND FRUITS (µg/kg)

PNA	Cabbage	Kale	Spinach	Lettuce	Tomatoes	Other Fruits	Salad
Benz(a)anthracene		43.6 - 230	16.1 (3)		0.3 (3)		4.6 - 15.4 (3)
Chyrsene		58.5 - 395	28.0 (3)		0.5 (3)		5.7 - 26.5 (3)
Benzo(a)pyrene	24.5 (26)	12.6 - 24.5 (25)	7.4 (25)	2.8 - 12.8 (25)	0.22 (25)	2 - 8 (3)	
		12.6 - 48.1 (3)	7.4 (3)		0.2 (3)		2.8 - 5.3 (3)

NOTE: Blanks indicate data not available.

TABLE 31. PNA CONCENTRATIONS IN COOKED, SMOKED, AND PROCESSED FOODS (µg/kg)

PNA	Refined oils or fats	Fresh fish frozen or salted	Broiled meat or fish	Smoked fish	Smoked meat sausages
Benzo(a)pyrene	0.9 - 15 (3)	<0.1 (27)	Meat and Sausages (3) 0.17 - 0.63	1.0 - 78.0 (23)	0.02 - 107 (3)
	Margarine 0.2 - 6.8 (3)			37 (23)	
	Coconut oil 43.7 (3)		BBQ meat (3) 2.6 - 11.2	0.1 - 0.8 (25)	
	Coconut fat 62 (3)		Fish 0.9 (3)	Traces - 2.1 (3)	
Chrysene	0.5 - 129 (3)		8.7 - 27.2 (29)		
			Ham (3) 0.5 - 2.6		
			Fish 4.3 (3)	0.3 - 173 (3)	
			Meat and sausages (3) 0.5 - 2.6		
			BBQ meat (3) 0.6 - 25.4		
Benz(a)anthracene	0.5 - 13.5 (3)		Meat and sausages (3) 0.2 - 1.1		Ham <12 (3)
	Coconut oil 98 (3)		Charcoal broiled (3) 1.4 - 31		0.02 - 189 (3)
	Coconut fat 125 (3)				

NOTE: Blanks indicate data not available.

(29) Shirotori, 1972.

TABLE 32. PNA CONCENTRATIONS IN BEVERAGES
(mg/m^3)

PNA	Roasted coffee	Teas	Whiskey
Benzo(a)pyrene	0.3 - 0.5 (25) 0.1 - 4 (3)	3.7 - 3.9 (25) 3.9 - 21.3 (3) Green teas (3) 0.5 - 16	0.04 (3)
Chrysene	0.6 - 19.1 (3)	4.6 - 6.3 (3)	0.04 - 0.06 (3)
Benz(a)anthracene	0.5 - 14.2 (3)	_[a]	0.04 - 0.08 (3)

[a]Data not available.

Fossil Fuels--
Levels of PNA's occurring in some fossil fuels and fuel fractions are shown in Table 33 (3). PNA's are more concentrated in fuel byproducts formed under high temperature conditions.

Population Exposed

There is indication of widespread exposure to PNA's from natural and anthropogenic sources. They occur in all phases of the environment. PNA's are more concentrated in urban areas where large population densities exist. Persons working with or using products derived from fossil fuels are potentially exposed to very high levels of PNA's.

TABLE 33. FOSSIL FUEL AND ITS DERIVATIVES (3)
(µg/kg)

PNA	Coal	Coal tar	Coal tar pitch	Petroleum asphalt	Creosote oil
Benzo(a)pyrene	300 - 1,000	30,000	12,500	0.1 - 27	0.00014 - 0.0002
Chrysene	_[a]	<2,860	<10,000	<0.4 - <34	<1,340
Benz(a)anthracene	_[a]	<6.980	<12,500	<35	<2,940

[a]Data not available.

HEALTH EFFECTS

PNA's are part of a group of known carcinogens that are present in the particulate phase of polluted air. The extent of the contribution of these agents to the incidence of human lung cancer, however, is unknown (30). The majority of health effects data

(30) Committee of Biologic Effects of Atmospheric Pollutants, National Research Council. Particulate Polycyclic Organic Matter. ISBN 0-309-02027-1 (PB-212 940), National Academy of Sciences, Washington, D.C., August 1972. 375 pp.

regarding PNA's is concerned with their carcinogenicity, mutagenicity and teratogenicity. Table 34 summarized the low toxic doses of selected PNA's (31)

TABLE 34. TOXICITY OF SOME PNA's (31)

Compound	Toxicity data (TD_{LO})[a] (route, animal, effect)
Anthracene	• 18 g/kg, oral, rat, carcinogenic • 3,300 mg/kg, subcutaneous, rat, neoplastic effects
Benzo(a)pyrene	• 2 µg/kg skin, mouse, carcinogenic • 250 µg/kg, subcutaneous, rate, neoplastic effects
Chrysene	• 200 mg/kg, subcutaneous, mouse, carcinogenic • 99 mg/kg for 31 weeks, intermittent, skin, mouse, neoplastic
Phenanthrene	• 700 mg/kg, oral, mouse, LD_{50} • 71 mg/kg, skin, mouse, neoplastic
Benz(a)anthracene	• 240 mg/kg for 5 weeks, skin, mouse, carcinogenic • 2 mg/kg, subcutaneous, mouse, carcinogenic • 10 mg/kg, intraveneous, mouse, lowest lethal dose • 8 mg/kg, parenteral, mouse, carcinogenic • 80 mg/kg, implant, mouse, carcinogenic
3-methycholanthrene	• 280 mg/kg, oral, rat, carcinogenic • 34 mg/kg for 25 weeks, intermittent, skin, rat, neoplastic • 18 mg/kg, subcutaneous, rat, carcinogenic • 39 mg/kg for 6 days, intraveneously, rat, neoplastic • 3 mg/kg, parenteral, rat, carcinogenic • 100 mg/kg for 5 weeks, intermittently, intratracheal, rat, carcinogenic • 800 µg/kg, implant, rat, carcinogenic • 40 mg/kg for 20 days of pregnancy, oral, mouse, neoplastics • 2,800 mg/kg for 90 days continuously, oral, mouse, carcinogenic • 13 mg/kg for 42 weeks, intermittently, skin, mouse, carcinogenic • 100 mg/kg for intraperitoneal, mouse, lowest lethal dose • 1,600 mg/kg for 20 weeks intermittently, intraperitoneal, mouse, neoplastic • 312 µg/kg, subcutaneous, mouse, carcinogenic • 120 mg/kg for week, intermittently, intratracheal, mouse, carcinogenic • 80 mg/kg, implant, mouse, neoplastic • 40 mg/kg, implant, dog, neoplastic • 100 mg/kg for 9 weeks, intermittently, intrapleural, rabbit, neoplastic • 132 mg/kg for 12 weeks, intermittently, intratracheal, rabbit, carcinogenic • 4 mg/kg intraperitoneal, guinea pig, carcinogenic • 40 mg/kg for 15 days, subcutaneous, guinea pig, carcinogenic • 36 mg/kg, intraveneously, guinea pig, neoplastic • 2,075 mg/kg for 17 weeks, intermittently, oral, hamster, carcinogenic • 3,320 µg/kg for 40 weeks, skin, hamster, neoplastic • 4,150 µg/kg, subcutaneous, hamster, neoplastic • 58 mg/kg, implant, hamster, carcinogenic • 4,500 µg/kg for 8 weeks, intermittently, intraperitoneal, chicken, carcinogenic • 27 mg/kg, intratracheal, duck, carcinogenic • 11 mg/kg, intrarenal, frog, lowest lethal dose
Benzo(k)fluoranthene	• 72 mg/kg for 9 weeks, skin, mouse, carcinogenic
Pyrene	• 10 µg/kg for 3 weeks, intermittently, skin, mouse, neoplastic
2,3-*o*-phenylenepyrene	• 72 mg/kg for 9 weeks, intermittently, subcutaneously, mouse, carcinogenic
1,2,5,6-dibenzanthracene	• 500 µg/kg, subcutaneous, rat, carcinogenic • 360 mg/kg for 22 weeks, continuously, oral, mouse, carcinogenic • 6 µg/kg, skin, mouse, neoplastic • 76 µg/kg, subcutanecus, mouse, carcinogenic • 10 mg/kg, intraveneously, mouse, lowest lethal dose • 80 mg/kg, implant, mouse, neoplastic • 30 mg/kg, intraveneously, guinea pig, neoplastic • 11 mg/kg, intramuscularly, pigeon, carcinogenic • 8 mg/kg, intrareneally, frog, carcinogenic

[a]Some observed doses are expressed as dependent on time.

(31) Christensen, Herbert E., Ed., Registry of Toxic Effects of Chemical Substances, 1976 Edition, Rockville, Md., U.S. Department of Health, Education and Welfare, 1976. 1245 pp.

The American Conference of Governmental Industrial Hygienists has adopted an eight hour work day limit of 200 $\mu g/m^3$ for coal tar pitch volatiles (benzene fractions containing compounds such as anthracene, benzo(a)pyrene, phenanthrene, acridine, chrysene, and pyrene) (1). The World Health Organization has recommended 0.2 mg/m^3 of PNA's as a maximum permissible concentration for human consumption. This is calculated as the sum of six compounds. The recommended benzo(a)pyrene limit for the sum was 0.0075 mg/m^3, and the recommended limit for all PNA's was 0.03 mg/m^3 (1).

SECTION 5

CONTROL TECHNOLOGY

Indications are that chlorination and ozonation of water supplies destroy PNA's (1); however, byproducts may be produced that are much more toxic when they are "destroyed" by chlorination. An assessment of the degradation products formed and their toxicity appears to be mandatory.

Emissions of PNA's from combustion sources can be reduced by increasing air-to-fuel ratios. Secondary combustion devices for flue gases would also reduce emissions. Particulate matter seems to be a method of transport for PNA's in the environment; thus, particulate controls should help in reducing emissions.

STATIONARY SOURCES

Benzo(a)pyrene (BaP) is chosen to be a typical PNA emission for the purposes of this section, since BaP emissions represent the most completely characterized PNA emission. The most important contributors of BaP emissions in heat and power generation are hand-fired coal furnaces and wood burning; thus, the preferred choice of control would be by alternative fuel sources. One might argue that substitution is the only means of control for these two sources, as neither is amenable to better engineering controls.

In regard to refuse burning, efficient incinerators are being installed for municipal, commercial, industrial, and apartment building sources. Relative contributions from these sources are diminishing in comparison to coal refuse banks. Existing burning began spontaneously. Federal regulations have been proposed for all burning coal refuse piles which will eliminate most emissions as these regulations are implemented.

BaP emissions from catalytic cracking in the petroleum industry apparently are receiving necessary action through utilizing carbon monoxide (CO) waste boilers for effective control (see Table 8). From Table 8 it is clear that CO waste-heat boilers have significant beneficial effects on BaP emissions and, thus, on other PNA emissions.

Much of the BaP produced at byproduct coke ovens quite likely could be removed in the byproduct stream, except for that

escaping from a leaky system. However, BaP emissions from most coke processing still appear to be quite high, whether they originate from charging or leaks or directly from the gas stream.

Some possible approaches to controlling BaP from coke ovens are under investigation by EPA and industry groups; two demonstration projects for particulate control from coke ovens are in progress, and BaP sampling is being done simultaneously (32).

Sampling results indicate that about 90% control of particulates is achieved (32). With this level of particulate control, a similar degree of reduction in BaP emissions was expected. Preliminary evaluation of the BaP fraction of the particulate from the controlled versus the noncontrolled larry car (vehicle that drops coal into the oven) indicates that approximately 85% to 90% control is achieved (32). If these results are obtained for other types of particulate control, a reduction of PNA's should result. These results confirm previous expectations of control engineers that particulate control will significantly reduce BaP emissions.

MOBILE

Before the current concern for reducing vehicle emissions was instigated by the Clean Air Act, most vehicles operated with fuel-rich carburetion to promote smooth performance and quick power response. Preliminary modifications prior to the 1970 Clean Air Amendments resulted in leaner fuel-air mixtures and lower BaP emissions.

Emission control devices will affect control of BaP concomitantly, as indicated in Table 35. Data to support this view are based on current exhaust sampling techniques. If such a high degree of control is achieved in actual practice, mobile source pollution caused by BaP will assume a much less significant role. At any rate, one may logically expect a reduction of BaP emissions from light-duty vehicles as a result of the EPA motor vehicle control activity. A higher degree of uncertainty exists for other transportation sources; e.g., buses, heavy diesel trucks, or aircraft.

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(32) Preferred Standards Path Report for Polycyclic Organic Matter. Draft report, U.S. Environmental Protection Agency, Durham, North Carolina, October 1974. 107 pp.

TABLE 35. AUTOMOTIVE BENZO(a)PYRENE EMISSION FACTORS (32)

Source	Benzo(a)pyrene emission factors (mg/m^3 of fuel consumed)
Uncontrolled car (1956-1964)	45
1966 uncontrolled car	5 to 21
1968 emission-controlled vehicle	2 to 6
Advanced systems[a]	0.5

[a]Catalytic converter or thermal reactor.

SECTION 6

REGULATORY ACTION

Limitation of carbon monoxide and hydrocarbon emissions from motor vehicles has simultaneously and dramatically reduced the emissions of PNA's. A 1974 analysis of stationary source problems concluded that control regulations designed specifically for benzo(a)pyrene or polynuclear aromatic hydrocarbons were not warranted or practical. It did note that compliance with existing regulations for incinerators, open burning, coal combustion, and coking operations could significantly reduce emissions. Additional efforts to document stationary source emissions, atmospheric chemistry, and human exposure have been initiated on a limited scale. Consideration is being given to establish revised standards for coke oven emissions under the Clean Air Act.

One hundred and twenty-nine chemicals including 13 polynuclear aromatic hydrocarbons, have recently been designated as priority pollutants for study. Physical and chemical behavior, health and environmental effects, and sources and environmental levels are to be documented. Appropriate water quality criteria, effluent guidelines, toxic pollutant standards, and/or pretreatment requirements will be established under the Federal Water Pollution Control Act in accordance with a court-approved schedule (33).

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(33) Identification of Selected Federal Activities Directed to Chemicals of Near-Term Concern. EPA 560/4-76-007, U.S. Environmental Protection Agency, Washington, D.C., September 1976. 21 pp.

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